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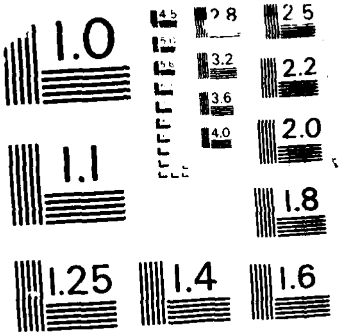
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# THE CORROSION RESISTANCE OF AN ALUMINUM ALLOY COATED WITH POLYSILAZANE DERIVED CERAMICS

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Contribution from the Organometallic and Inorganic
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## ABSTRACT

Aluminum plates were dip-coated in a poly-N-methylsilazane, -$[H_2SiNCH_3]_n$-, solution. Heating process at 400°C transformed the inorganic polymer into coatings that exhibited good corrosion resistance characteristics in a marine environment relative to the bare metal as measured and interpreted by electrochemical methods.

The corrosion rate was inhibited by almost one order of magnitude. No microscopic degradation of the coatings was observed after 21 days of measurement, which confirms the stability of the coatings as determined by the electrochemical technique.

The recent development of high-tech ceramic materials with improved properties or reduced fabrication costs represents one of the most advanced technologies in contemporary materials science. New applications for ceramic materials have proliferated along with this development, and ceramics are now considered as replacements for high performance alloys and plastics in many service environments [1].

Corrosion-resistant ceramic coatings on metallic substrates is a major potential application derived from chemical routes. In many instances, ceramic-coated metals and alloys not only are an attractive alternative to either ceramic monolith or metallic structures but also office advantages of both. For example, ceramic-coated metallic substrates the same abrasion and corrosion resistance of monolithic ceramic structures in harsh environments without the drawback of low toughness and high cost. Further, the coatings can be applied to a metal shape after machining and joining operations are complete.

Ceramic coatings on substrates have not been widely deployed for several reasons. First, coatings must adhere well and have the right expansion coefficient, especially during temperature cycling; otherwise, spallation will occur. Second, many ceramics coatings can be applied and processed as coatings only at high temperatures (>1100°C) using the expensive and time-consuming method of chemical vapor deposition (CVD) [2]. Therefore, aluminum alloys and other low melting point materials are not easily protected.

We recently developed a new, low temperature method for preparing and applying adherent, corrosion-resistant ceramic coatings on a variety of engineering alloy and composite substrates using tractable preceramic polymer "paint" solutions. This coating process was used extensively to prepare amorphous silicon nitride ($Si_3N_4$) type coatings on an aluminum alloy 6061 substrate to improve its corrosion resistance. This brief communication compares the corrosion resistance of coated and uncoated aluminum 6061 T6 alloy using AC impedance spectroscopy and Tafel extrapolation methods.

## Procedure

A series of novel polysilazanes [3,4] were developed that can be dipcoated, sprayed, or spincoated onto metallic surfaces. These precursor coatings can be transformed into ceramic coatings by heating (pyrolyzing) to temperatures as low as 400°-500°C, well below the melting or softening points of many high performance alloy and composite substrates. The product coatings are amorphous ceramic materials, rich in silicon and nitrogen, that ultimately transform to $Si_3N_4$ when heated at elevated temperature. Briefly, aluminum alloy 6061 T6 is dipcoated in a 10 wt% solution of poly-N-methylsilazane (PNMS) consisting mainly of $-[H_2SiNCH_3]_x-$ units in tetrahydrofuran (THF) solvent containing a cross-linking catalyst. Then the sample is heated to 400°C under nitrogen to give a coating of approximately 1-2 μm thick. The coatings cannot be removed in tape pull tests, but at this thickness, they can be scratched with metallic objects. When the coatings are poorly prepared, they contain microcracks readily visible by optical microscopy, but under some conditions, coatings exhibit no microcracks or pores even at highest magnification under scanning electron microscopy (1-μmscale). Thus, the application procedures have not yet been fully optimized.

In this work, AC impedance spectra for both coated and uncoated aluminum 6061 T6 alloy were recorded with a Solartron 1250 Frequency Response Analyzer (FRA). The FRA was controlled by a MacIntosh Plus computer via an IEEE 488 interface bus. Data were recorded over a range of frequencies from about 10 kHz to about 5 mHz. A 10-mV rms sine wave perturbation from the FRA was superimposed on an applied DC bias from a PAR Model 173 potentiostat. The DC bias was set at the corrosion potential of the coated and uncoated material in deaerated 3.5% NaCl solution at pH 6.4 before each measurement. The FRA potential and current input leads were taken directly from a conventional three-electrode cell and not from the potentiostat electrometer and current output jacks. All potentials are reported relative to a saturated calomel reference electrode (SCE).

Potentiodynamic polarization sweep experiments on ceramic coated and uncoated 6061 T6 samples in the deaerated NaCl solution were performed with a PAR Model 350 Corrosion Measurement System. The solution was deaerated to facilitate the measurement of the cathodic Tafel slope. A sweep rate of 1 mV/s was used for both anodic and cathodic polarization sweeps from the corrosion potential. The uncoated sample surfaces were prepared by abrasive polishing to 0.3-μm alumina powder. The edges of both coated and uncoated samples were masked with Amercoat 90 paint.

## Results

The Tafel extrapolation method was used on the cathodic portion of the polarization diagrams to estimate corrosion rates based on the geometric surface area. Figure 1 shows the cathodic curves for an uncoated, freshly polished 6061 T6 alloy sample and a coated 6061 T6 sample that had been exposed to the deaerated NaCl solution for 29 days. The corrosion potential for the coated sample was about 130 mV more positive than the uncoated sample, but the Tafel slope was almost twice that of the uncoated sample (340 mV/decade compared with 175 mV/decade). Corrosion currents were calculated by Tafel extrapolation to the corrosion potential from the cathodic portion of the polarization curves. The anodic Tafel slopes were assumed to be equal to infinity since aluminum alloys are passivated under these experimental conditions. Corrosion currents were 1.4 $\mu A/cm^2$ and 7.4 $\mu A/cm^2$ for the coated and uncoated specimens, respectively, or roughly five times smaller for the coated, aged sample.

The polarization curves in Figure 1 show that over a wide potential range the coated surface is less catalytic than the uncoated surface to the hydrogen evolution reaction. However, it is possible that the hydrogen evolution reaction is localized at the base of the microcracks in the coating and that the local current density in these cracks is substantially higher than the 1.4 $\mu A/cm^2$ calculated by Tafel extrapolation. If this is the case, then further development of the coating process is needed to reduce or eliminate the microcracks in the coating, which may lead to further improvements in corrosion resistance.

The anodic portions of the polarization diagrams were also recorded to compare the pitting potentials for the coated and uncoated samples. Figure 2 shows that the pitting potential of the uncoated sample is approximately -0.750 V/SCE compared with +0.800 V/SCE for the coated, aged sample. The pitting potential of the coated sample is increased by more than 1-V by the ceramic coating despite the possibility of microcracks in the coating. Apparently, localized acidification of the solution within microcracks does not readily occur and the pit nucleation process is retarded. In fact, optical examination of the coated sample after this test showed that microcraks were present in the coating but pits were dispersed across the entire substrate surface with only a slight preference for nucleation at the cracks. This observation suggests that the localization of current at microcracks might not readily occur. Perhaps the substrate is coated with the ceramic product even at the base of the microcracks and the NaCl solution hydrates the coating somewhat uniformly to your access to the aluminum alloy substrate.

AC impedance spectra were recorded periodically on a $Si_3N_4$-coated sample during a three-week exposure in the deaerated NaCl solution to study the longer term behavior of the coatings in situ. Figures 3 and 4 show the impedance spectra for this sample, represented as Bode plots, after 5 hours and 21 days in solution, respectively. In these Figures, /Z/ represents the impedance magnitude, $\omega$ represents the angular frequency ($2\pi$), and the phase angle is defined as the arc tangent of the ratio of imaginary/real parts of the electrode impedance.

Both Figures 3 and 4 have similar characteristics. In both cases, two relaxations occur within the observable frequency range, as indicated by the double peaks in the phase angle curves. Further, low-frequency impedance magnitudes are similar, suggesting that corrosion rates based on geometric surface areas are similar. Polarization resistances were approximated as at least 32,000 ohms, and corrosion currents were calculated from the Stern-Geary relationship and the cathodic Tafel slope reported above. The corrosion rate of the coated sample was determined to be at most 2.6 $\mu A/cm^2$ and was relatively independent of time during the three-week exposure. This value compares well with the 1.4 $\mu A/cm^2$ determined by the Tafel extrapolation method described above. However, it is again possible that the relaxation processes observed in Figures 3 and 4 are localized at microcracks in the coating and that corrosion current densities may be higher at these locations.

AC impedance spectra were also recorded on uncoated 6061 T6 aluminum alloy for comparison with the coated sample impedances. Figure 5 shows that the two relaxations are similar to those observed in Figures 3 and 4 for the coated sample. The low-frequency impedance magnitude shown in Figure 5 was used to estimate the maximum corrosion rate of the uncoated sample as described above. A corrosion rate of almost 22.6 $\mu A/cm^2$ was calculated. This value is about three times larger than the value (7.4 $\mu A/cm^2$) calculated by Tafel extrapolation methods, but is almost an order of magnitude larger than the value of 2.6 $\mu A/cm^2$ calculated for the coated sample using AC impedance spectroscopy.

In summary, $Si_3N_4$ ceramic coatings have been applied to 6061 T6 aluminum alloy substrates using a new low temperature ceramic coating application process. The coated, 6061 T6 aluminum alloy substrates exhibit corrosion rates and hydrogen evolution rates that are five to ten times lower than an uncoated specimen. The corrosion protection afforded by these $Si_3N_4$ coatings does not degrade significantly either physically or chemically with time up to at least 21 days, and the coated material is substantially more resistant to pitting corrosion.

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# CAPTIONS

Figure 1 Cathodic Polariation Diagram

Figure 2 Anodic Polarization Diagram

Figure 3 AC Impedance Spectrum of Coated 6061 Aluminum Alloy in 3.5% NaCl for 5 hours

Figure 4 Coated 6061 Alloy in 3.5% NaCl for 21 days

Figure 5 AC Impedance Spectrum of 6061 Aluminum Alloy in 3.5% NaCl for 3 hours

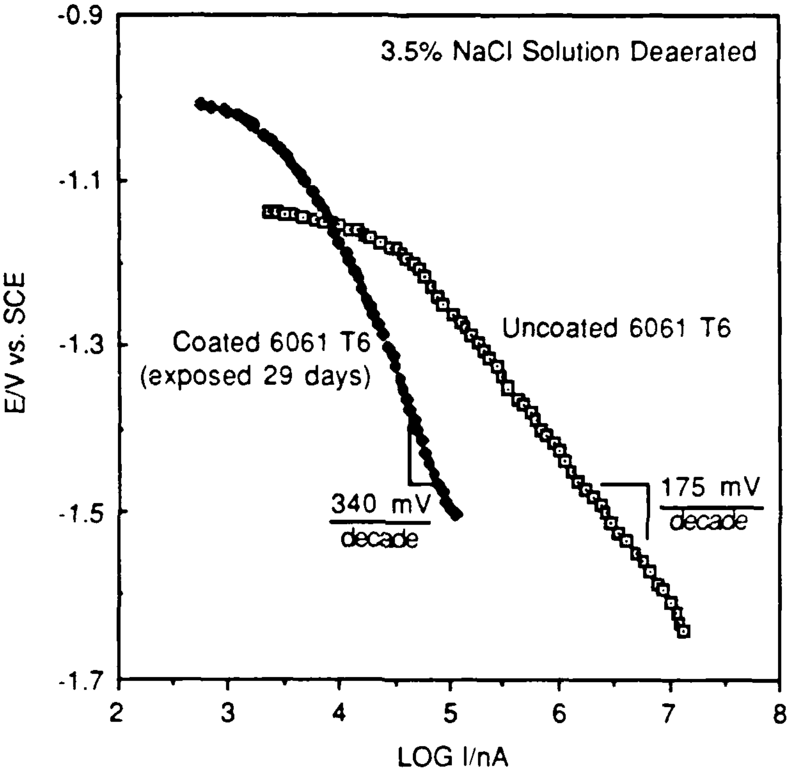

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FIGURE 1 CATHODIC POLARIZATION DIAGRAM

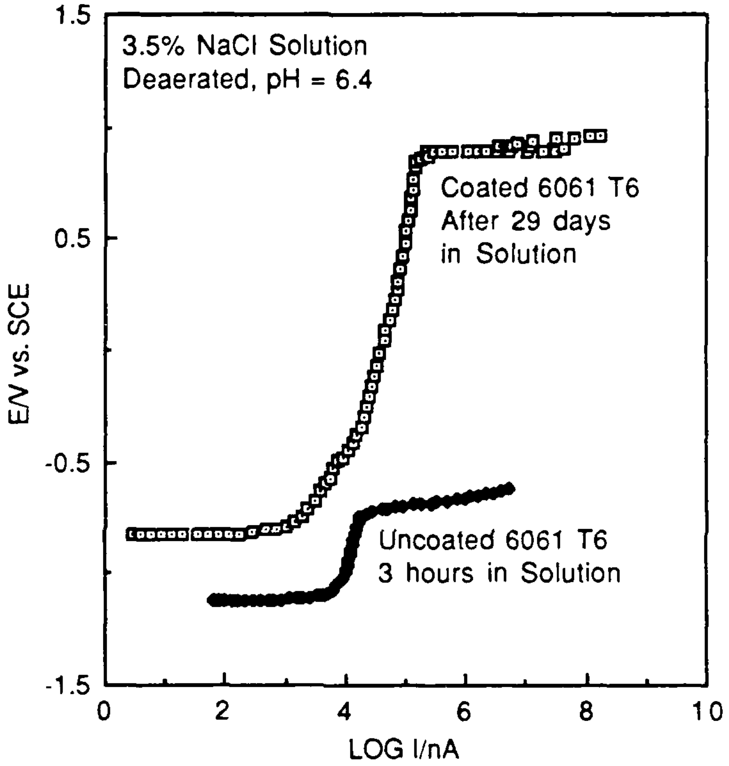

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FIGURE 2 ANODIC POLARIZATION DIAGRAM

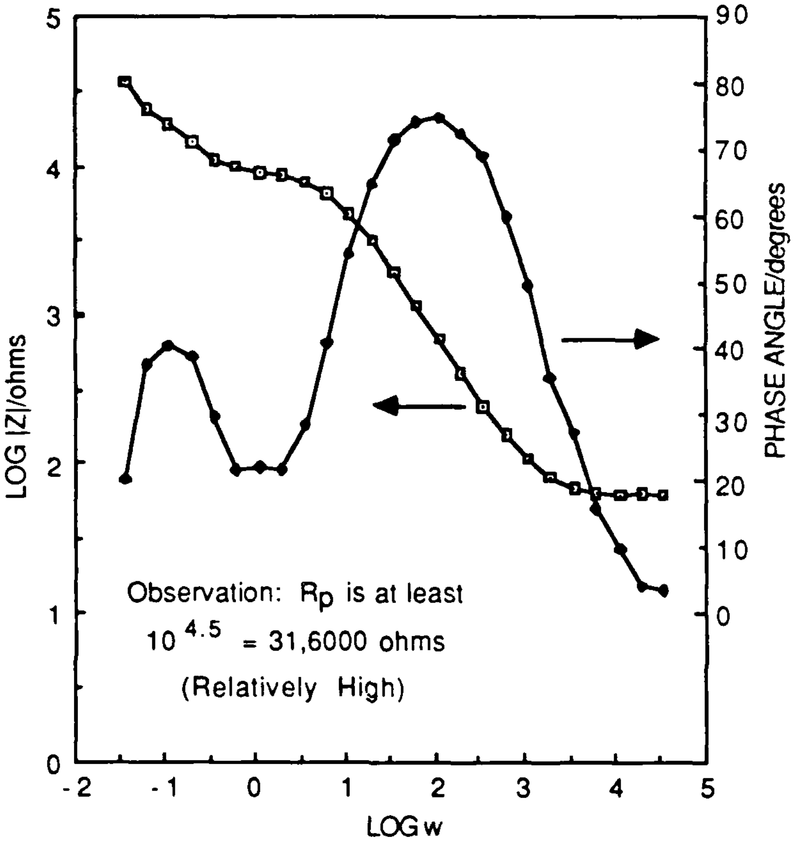

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FIGURE 3 AC IMPEDANCE SPECTRUM OF COATED 6061 ALUMINUM ALLOY IN 3.5% NaCl FOR 5 HOURS

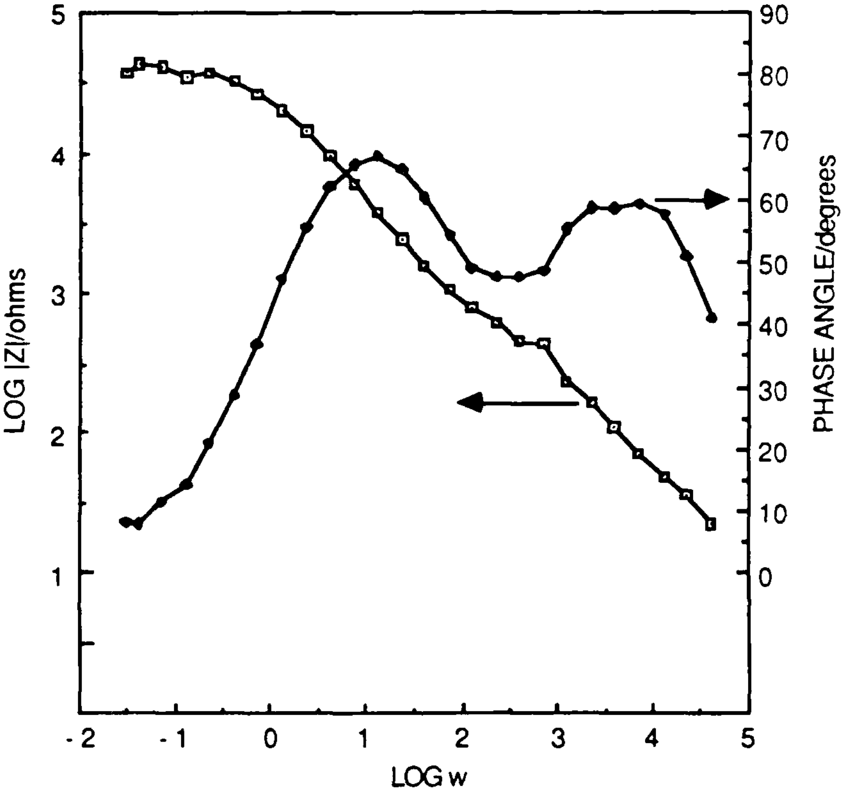

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FIGURE 4 COATED 6061 ALLOY IN 3.5% NaCl FOR 21 DAYS

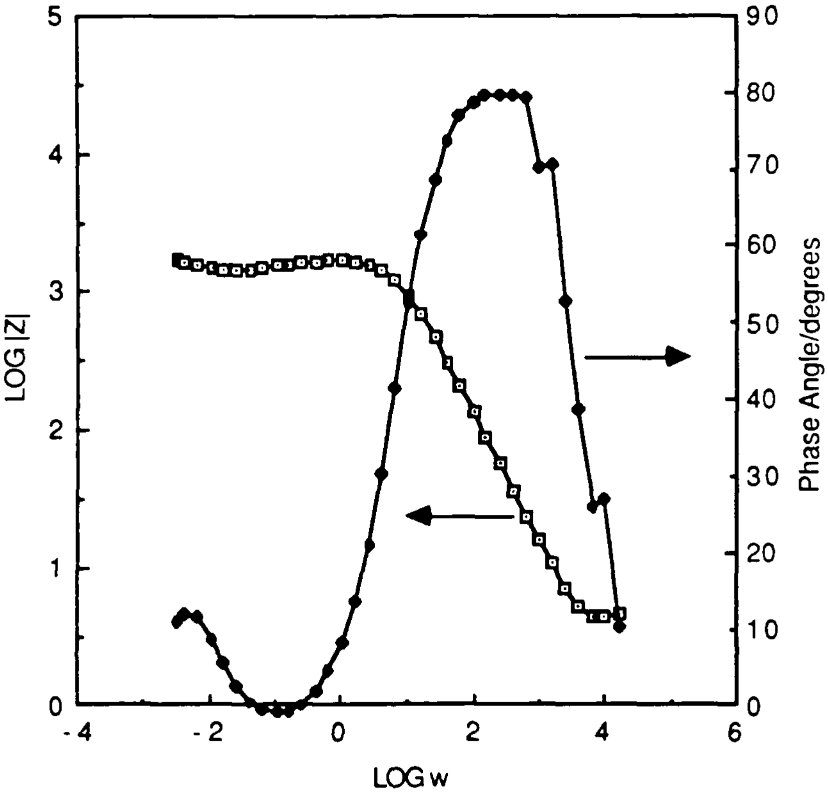

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FIGURE 5 AC IMPEDANCE SPECTRUM OF 6061 ALUMINUM ALLOY IN 3.5% NaCl FOR 3 HOURS

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